

Intermediate-spin state and properties of LaCoO_3

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Abstract

The electronic structure of the perovskite LaCoO_3 for different spin states of Co ions was calculated in the LDA+U approach. The ground state was found to be a nonmagnetic insulator with Co ions in a low-spin state. Somewhat higher in energy we found two intermediate-spin states followed by a high-spin state at significantly higher energy. The calculation results show that Co $3d$ states of t_{2g} symmetry form narrow bands which could easily localize whilst e_g orbitals, due to their strong hybridization with the oxygen $2p$ states, form a broad σ^* band. With the increase of temperature which is simulated by the corresponding increase of the lattice parameter, the transition from the low- to intermediate-spin states occurs. This intermediate-spin (occupation $t_{2g}^5 e_g^1$) can develop an orbital ordering which can account for the nonmetallic nature of LaCoO_3 at $90 \text{ K} < T < 500 \text{ K}$. Possible explanations of the magnetic behavior and gradual insulating-metal transition are suggested.

1 INTRODUCTION

Among the systems showing semiconductor to metal transition LaCoO_3 is especially interesting due to the fact that it also displays very unusual magnetic behavior, often associated with low-spin (LS) – high-spin (HS) transition [1]. Although a large number of investigations have been carried out since the early 1960's the character of the transition and the nature of the temperature dependence of the spin state is still unclear. For example the temperature dependence of the magnetic susceptibility shows a strong maximum at around 90 K followed by a Curie-Weiss-like decrease at higher temperatures [2] which was interpreted by the authors as a LS to a HS transition. The semiconductor to metal-like transition occurs in a range of 400 – 600 K, well above this transition. The insulating nature of LaCoO_3 below 400 – 600 K was attributed by Raccach and Goodenough to an ordering of LS and HS Co^{3+} ions in a NaCl like structure [1], with the itinerant electrons in a broad band formed by the transition metal e_g orbitals. This structural change however has not been observed in crystallographic studies. Recent neutron scattering experiments [3] suggest that the semiconductor – metal transition is not predominantly magnetic in origin but a clear picture of what its nature is absent.

Photoemission (XPS) and X-ray absorption (XAS) studies on the other hand have been interpreted in terms of a spin change at the semiconductor – metal transition [4]. There are however several discrepancies in the interpretation. The Co $2p$ XAS line shape at room temperature looks like LS Co^{3+} which is not consistent with

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a spin state transition at 90 K. However, the valence band XPS spectrum at 300 K is quite different from that of a HS compound. So the interpretation of the two transitions is still uncertain.

In most of the previous studies one has assumed a rather ionic and ligand field-like starting point. In this picture the possibility of intermediate spin (IS) states as well as local symmetry lowering, orbital ordering and the large bandwidth of the e_g states were not considered. It has recently been pointed out by several authors that the oxides corresponding to high formal oxidation states may be negative charge transfer systems in the Zaanen-Sawatzky-Allen scheme [5] resulting in an essential modification of the electronic structure, in particular in a possible stabilization of an IS states [6].

A first physical model to explain the transitions in LaCoO_3 was proposed and recently revised by Goodenough in [1]. It was suggested that for trivalent cobalt in LaCoO_3 the crystal field energy Δ_{cf} is only slightly larger than the intraatomic (Hund) exchange energy Δ_{ex} . Thus the ground state of the Co ion is LS 1A_1 (S=0) and the excited HS state 5T_2 (S=2), according to [1], is only 0.08 eV higher in energy. The corresponding one-electron configurations are $t_{2g}^6 e_g^0$ for the LS state and $t_{2g}^4 e_g^2$ for the HS state. The increase in temperature leads to the population of the HS states which is reflected in the magnetic susceptibility measurements. The semiconductor-metal transition was interpreted in a rather vague way as a formation of a σ^* band from the localized ionic e_g states. Long-range order of the LS and HS Co ions was assumed based on the results of the X-ray diffraction measurements. The recent neutron diffraction experiments [3] did not confirm it, but did not exclude a short-range order.

The theoretical description of LaCoO_3 is a difficult task, because this system exhibits transition from the localized to the delocalized behavior, and the two main existing methods: one-electron band structure calculations based on the Local Density Approximation (LDA) and "model hamiltonian configuration interaction" approach (which were both used for the compound under consideration [4, 7]) were constructed for the, respectively, completely itinerant and fully localized cases.

Recently a paper of Sarma *et al* was published [8] where the results of the LSDA calculations for LaMO_3 ($M=\text{Mn, Fe, Co, Ni}$) were presented. It was claimed there that LSDA results gave good agreement with the X-ray photoemission spectra. Such an agreement is not necessary a proof of the adequate description of the electronic structure. A well known example is NiO, where LSDA gives a sharp peak at the top of the valence band in agreement with XPS, but the nature of this peak is Ni3d t_{2g} minority-spin character, while it is generally accepted that this peak is derived from $d^8\bar{L}$ final state. The real proof of the correctness of the one-electron approximation would be an absence of the satellites in the photoemission spectra. Also the XPS spectra, with which a comparison was made in [8], were measured at the room temperature, where LaCoO_3 is already not in the low-spin state. So XPS must be compared with LSDA result corresponding to the magnetic solution and not a non-magnetic one as in [8].

Anisimov *et al* proposed a so-called LDA+U method [9] which combines in one calculation scheme LDA and Hubbard model approaches and is able to treat on a "first-principle" basis the systems with strong Coulomb correlation. It was demonstrated that this method (in contrast to standard LDA) could describe the existence of the different states of the system under consideration which are close in total energy (holes in doped copper oxides [10] and transition metal impurities in insulators [11]).

In this paper we present a study of an electronic structure of LaCoO_3 in the LDA+U approach. In contrast to the standard LDA there are several stable solutions corresponding to different local minima of the LDA+U functional. We have found a nonmagnetic insulating ground state in agreement with the experiment. We have also found two orbitally-polarized magnetic solutions corresponding to IS states (one of them is gapless semiconductor and the other is metal) and semiconducting magnetic solution corresponding to a HS state of the system, which lies much higher in energy. In addition we found that the e_g states form broad bands whereas the t_{2g} states exhibit narrow bands, split by Coulomb interactions into the lower (occupied) and upper (unoccupied) Hubbard bands. Using the results of these calculations, we propose an interpretation of the behavior of LaCoO_3 . According to our scheme, there first occurs with increasing temperature a transition from a LS (nonmagnetic) insulating ground state to a state with an IS (configuration $t_{2g}^5 e_g^1$). Due to strong Jahn-Teller nature of this configuration, this state may develop orbital ordering. The orbitally-ordered state turns out to be nonmetallic (actually nearly zero-gap semiconductor) in our calculations. With the further increase of the temperature the orbital ordering

may be gradually destroyed which can explain the transition to a metallic state observed in LaCoO_3 at 400 – 600 K. We hope that this new information will eventually lead to a better understanding of LaCoO_3 and other similar materials.

2 CALCULATION METHOD

The LDA+U method [9] is based on the assumption that it is possible to separate all electrons in the system in two subsets: the localized states (for LaCoO_3 these are the Co $3d$ -orbitals), for which Coulomb intrashell interactions are described by the Hubbard-like term, and the itinerant states, where the averaged LDA energy and potentials are good approximations.

It is known that LDA calculations can provide all the necessary model parameters (such as the Coulomb parameter U [12], the exchange J , hopping parameters describing hybridization *etc.*) on a first-principle basis, but the one-electron structure of the LDA equations with the orbital-independent potential does not allow to use these parameters in the full variational space. LDA+U overcomes this problem by using the framework of the degenerate Anderson model in the mean-field approximation. In this method, the trial function is chosen as a single Slater determinant, so it is still a one-electron method, but the potential becomes orbital-dependent, and that allows one to reproduce the main features of strongly correlated systems: the splitting of the d -band to the occupied lower Hubbard band and unoccupied upper Hubbard band.

The main idea of our LDA+U method is that the LDA gives a good approximation for the average Coulomb energy of d - d interactions E_{av} as a function of the total number of d -electrons $N = \sum_{m\sigma} n_{m\sigma}$, where $n_{m\sigma}$ is the occupancy of a particular $d_{m\sigma}$ -orbital:

$$E_{av} = U \frac{N(N-1)}{2} - J \frac{N(N-2)}{4}. \quad (1)$$

But LDA does not properly describe the full Coulomb and exchange interactions between d -electrons in the same d -shell. So we suggested to subtract E_{av} from the LDA total energy functional and to add orbital- and spin-dependent contributions to obtain the exact (in the mean-field approximation) formula:

$$E = E_{LDA} - \left(U \frac{N(N-1)}{2} - J \frac{N(N-2)}{4} \right) + \frac{1}{2} \sum_{m,m',\sigma} U_{mm'} n_{m\sigma} n_{m'-\sigma} + \frac{1}{2} \sum_{m \neq m', m', \sigma} (U_{mm'} - J_{mm'}) n_{m\sigma} n_{m'\sigma}. \quad (2)$$

The derivative of Eq.(2) over orbital occupancy $n_{m\sigma}$ gives the expression for the orbital-dependent one-electron potential:

$$V_{m\sigma}(\vec{r}) = V_{LDA}(\vec{r}) + \sum_{m'} (U_{mm'} - U_{eff}) n_{m'-\sigma} + \sum_{m' \neq m} (U_{mm'} - J_{mm'} - U_{eff}) n_{m\sigma} + U_{eff} \left(\frac{1}{2} - n_{m\sigma} \right) - \frac{1}{4} J. \quad (3)$$

The Coulomb and exchange matrices $U_{mm'}$ and $J_{mm'}$ are:

$$U_{mm'} = \sum_k a_k F^k, \quad (4)$$

$$J_{mm'} = \sum_k b_k F^k, \quad (5)$$

$$a_k = \frac{4\pi}{2k+1} \sum_{q=-k}^k \langle lm | Y_{kq} | lm \rangle \langle m' | Y_{kq}^* | lm' \rangle, \quad (6)$$

$$b_k = \frac{4\pi}{2k+1} \sum_{q=-k}^k |\langle lm | Y_{kq} | lm' \rangle|^2, \quad (7)$$

Table 1: Basis set and MT-sphere radii used in the calculation.

Atom	$\kappa_1^2 = -0.01$ Ry	$\kappa_2^2 = -1.0$ Ry	$\kappa_3^2 = -2.3$ Ry	R_{MT} , Å
La	<i>6s6p5d4f</i>	<i>6s6p5d4f</i>	<i>6s6p5d</i>	1.77
Co	<i>4s4p3d</i>	<i>4s4p3d</i>	<i>4s4p</i>	1.26
O	<i>2s2p</i>	<i>2s2p</i>	<i>2s</i>	0.66

where the F^k are Slater integrals and $\langle lm|Y_{kq}|lm'\rangle$ are integrals over products of three spherical harmonics Y_{lm} .

For d -electrons, one needs F^0, F^2 and F^4 and these can be linked to the parameters U (direct Coulomb interaction) and J (intraatomic exchange) obtained from the LSDA-supercell procedures [12] via $U = F^0$ and $J = (F^2 + F^4)/14$, while the ratio F^2/F^4 is to a good accuracy constant ~ 0.625 for $3d$ elements [13]. For LaCoO_3 , the Coulomb parameter U was found to be 7.8 eV and the exchange parameter $J=0.92$ eV.

The LDA+ U approximation was applied to the full potential linearized muffin-tin orbitals (FP-LMTO) calculation scheme [14]. Crystallographic data being used in the calculations were taken from [3]. According to them, LaCoO_3 has a pseudocubic perovskite structure with a rhombohedral distortion along the (111) direction. The unit cell contains two formula units. Since this rhombohedral distortion is small (the largest rhombohedral angle is 60.990° at 4 K), we use the conception of t_{2g} and e_g orbitals, as referred to in the cubic setting in the following discussion. Temperature was introduced in our calculations only by the change of lattice parameter and atomic positions according to the data of Ref.[3]. The most detailed description of the technical aspects of FP LMTO calculations for the perovskite-type complex oxides can be found in [15]. The optimal choice of the basis set for describing the valence band and the bottom of conduction band of the LaCoO_3 is presented in Table 1. Since U -correction is applied for the Co d -orbitals, the value of the *muffin-tin* (MT) radius for Co was chosen close to its value in metallic Co in order to get the full $3d$ -density inside the sphere. For the correct description of the wave functions in the interstitial region, we expanded the spherical harmonics up to the value of $l_{max}=5, 4, 3$ for La, Co and O MT-spheres correspondingly. The Brillouin zone (BZ) integration in the course of the self-consistency iterations was performed over a mesh of 65 \mathbf{k} -points in the irreducible part of the BZ. Densities of states (DOS) were calculated by the tetrahedron method with 729 \mathbf{k} -points in the whole BZ.

As the potentials for the various d -orbitals of Co are different in LDA+ U , it is not obvious *a priori* what will be the final symmetry of the system under consideration. In preliminary calculations we assumed for the simplicity that LaCoO_3 has a perfect perovskite-type cubic lattice. To allow the system to choose the appropriate symmetry by itself, we perform an integration not over 1/48 part of BZ as for cubic symmetry but over 1/8 (D_{2h} symmetry group). The resulting symmetries were found to be cubic O_h for the ground (LS) state and tetragonal D_{4h} for the excited states. Practically the same situation occurs in real $R\bar{3}c$ symmetry: the occupancies of xy, yz, zx orbitals are about the same for the low-spin configuration as well as that of $3z^2 - r^2, x^2 - y^2$ orbitals. The degeneracy of xy and yz, zx orbitals is broken in the other spin states.

3 RESULTS AND DISCUSSION

3.1 Homogeneous Solutions

We start by considering the results of the calculations for homogeneous regimes, without extra superstructure. The possibility to get a solution with an orbital ordering is considered in section 3.2.

The detailed results of the calculations with crystallographic data corresponding to 4 K are presented in Table 2. One must start with the equal occupancies of all three t_{2g} orbitals and also of two e_g orbitals (e.g. $t_{2g}^6 e_g^0$) to obtain the LS configuration. The initial spin polarization vanished during self-consistency iterations resulting in a nonmagnetic final solution. The charge excitation spectrum has a semiconducting character in accordance with experimental data [16] (and in contrast to the LDA result [7]) with the energy gap equal to 2.06 eV. The top of the valence band (Fig.1) is formed by the mixture of oxygen $2p$ states with Co t_{2g} orbitals and the bottom

Table 2: Total energy difference, character of energy spectrum, occupancies of various d -orbitals of Co and magnetic moments for various Co spin-states in LaCoO_3 .

configu- ration	δ^a (eV)	energy gap (eV)		d-occupancies						μ_{d-Co} (μ_B)
$t_{2g}^6 e_g^0$	–	2.06	\uparrow, \downarrow	xy	yz	zx	$3z^2 - r^2$	$x^2 - y^2$	total	0
low-spin										
$t_{2g}^5 \sigma^*$	0.24	0 ^b	\uparrow	0.98	0.98	0.98	0.84	0.84	7.13	2.11
intermediate-spin			\downarrow	0.07	0.98	0.99	0.23	0.24		
$t_{2g}^4 e_g^2$	0.65	0.13	\uparrow	0.99	0.99	0.99	1.00	1.00	6.78	3.16
high-spin			\downarrow	0.99	0.08	0.11	0.33	0.30		

^a Total energy difference relative to the energy of $t_{2g}^6 e_g^0$ configuration.
^b Half-metal. Total magnetic moment per unit cell is 2 μ_B .

of conduction band predominantly by the e_g orbitals.

From the X-ray photoemission and absorption spectra [4] the gap was estimated to be 0.9 ± 0.3 eV. The optical measurements [17] gave ≈ 0.5 eV. The larger value of the calculated gap can be explained by the well known fact that a mean-field approximation, which is the basis of our LDA+U approach, usually overestimates the tendency to localization and hence the values of the gap.

The aim of our work was to find solutions corresponding to the higher-spin states of Co ions. Usually the HS state is described as a $t_{2g}^4 e_g^2$ configuration with the maximum value of spin $S=2$ (magnetic moment $\mu_{Co}=4 \mu_B$). This corresponds to the purely ionic model, and hybridization of the Co $3d$ -orbitals with the oxygen $2p$ -orbitals and band formation in a solid can renormalize significantly this ionic value. Such kind of renormalization was obtained in our calculations (see Table 2). The initial $t_{2g}^4 e_g^2$ configuration (two holes on d_{xz}^\downarrow , d_{yz}^\downarrow orbitals of the t_{2g} set and two on $d_{3z^2-r^2}^\downarrow$, $d_{x^2-y^2}^\downarrow$ of the e_g set with spin-down (minority) spin projection) results in the self-consistent solution with a magnetic moment of $\mu_{d-Co}=3.16 \mu_B$. The total energy of this HS solution is 0.65 eV per formula unit higher than the ground state LS $t_{2g}^6 e_g^0$ configuration. The unexpected result is that there exists an *intermediate-spin* solution (second line in Table 2, magnetic moment value $\mu_{d-Co}=2.11 \mu_B$) which is lower in total energy than the HS solution (0.24 eV per formula unit relative to the LS ground state). This solution was obtained when we started from the initial configuration $t_{2g}^5 e_g^1$, where only one electron was transferred from the t_{2g} to e_g states. The final self-consistent configuration is better described as a t_{2g}^5 state with a partially filled σ^* -band ($t_{2g}^5 \sigma^*$) with the occupancies of the $d_{3z^2-r^2}^\uparrow$ and $d_{x^2-y^2}^\uparrow$ orbitals equal to 0.84. In a configuration interaction language used in the cluster calculations this may be compared to a $d^6 + d^7 \underline{L}$ state where \underline{L} denotes a hole on the oxygen.

The IS state in our calculations turns out to be metallic (see, however, section 3.2), and HS state is semi-conducting (Fig.2,3). The reason for this is that the antibonding σ^* band (formed by e_g orbitals) is very broad and the band splitting is not strong enough to create a gap in the case of IS state. When the e_g^\uparrow band becomes completely filled (HS state), a small gap between e_g^\uparrow and e_g^\downarrow bands appears.

In Table 2 the occupation of different orbitals in different configurations is presented. One notices that the actual occupation is different from the formal "chemical" one and corresponds on the average not to 6 but rather to 7 electrons in d -shell. The reason for this is the strong hybridization of the empty e_g orbitals with oxygen $2p$ -orbitals. In the LS ground state every e_g orbital, which is formally empty, has actually an occupancy of about 0.33 resulting in 1.3 additional d -electrons above the formal six-electron configuration. In the case of excited IS state we have partially filled broad σ^* -band with the total number of e_g electrons increased by 0.85 as compared to the LS state and the number of t_{2g} -electrons 0.92 less than in LS state with as a result practically unchanged total number of d -electrons. Therefore, we used the notation $t_{2g}^5 \sigma^*$ in the Table 2 to prevent misunderstanding and in accordance with notation proposed in [1]. One may also say that despite the formal oxidation state Co^{3+} the real configuration e.g. in the IS state is a mixture of $t_{2g}^5 e_g^1$ and $t_{2g}^5 e_g^2 \underline{L}$ configurations.

Some other points concerning the results obtained are worth mentioning. As one can see from Fig.1, the

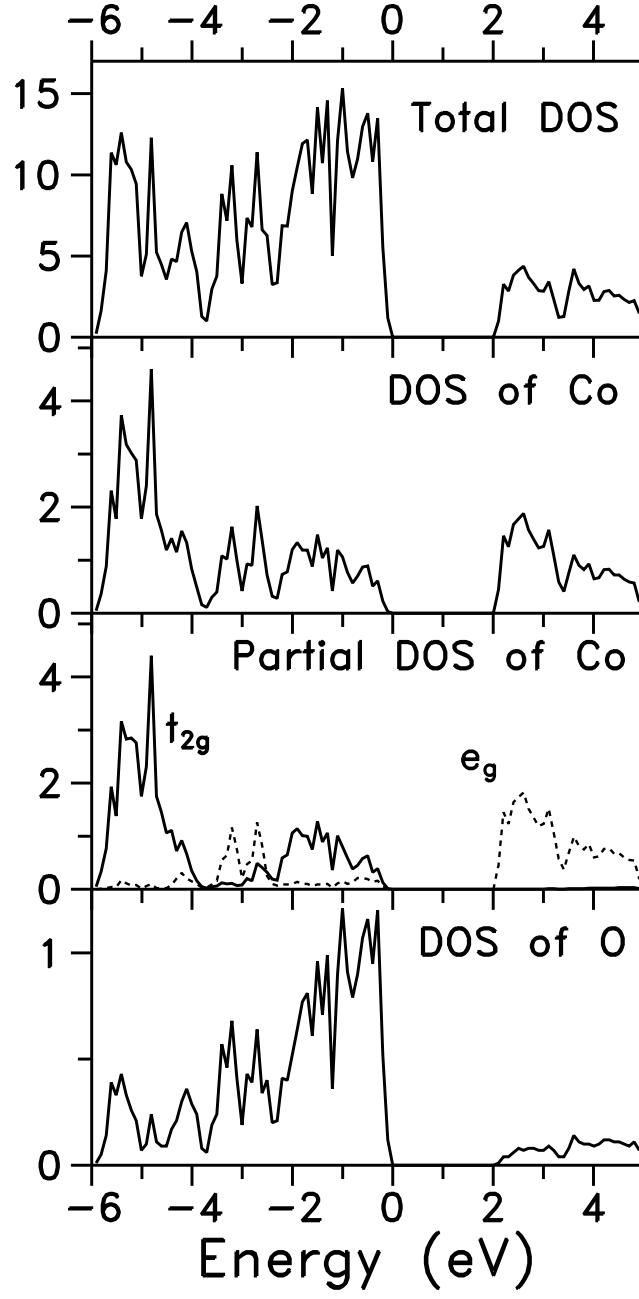


Figure 1: The total and partial densities of states obtained in LDA+U calculations for LaCoO_3 with Co ions in low-spin state ($t_{2g}^6 e_g^0$ configuration). For d -Co partial density of states solid line denotes t_{2g} orbitals and dashed line - e_g orbital.

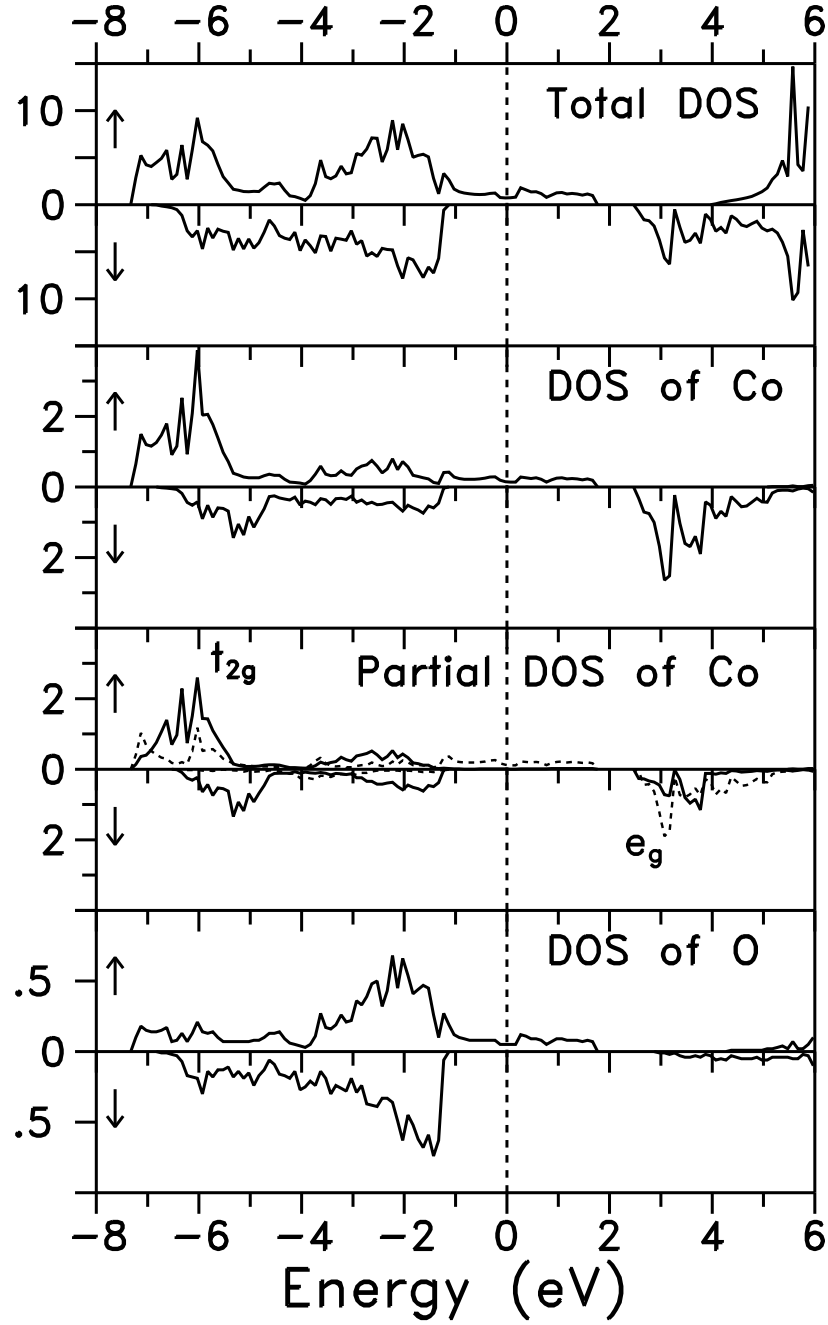


Figure 2: The total and partial densities of states obtained in LDA+U calculations for LaCoO_3 with Co ions in intermediate-spin state ($t_{2g}^5\sigma^*$ configuration). Fermi level is denoted by vertical dashed line. Arrows corresponds to spin-up and spin-down spin projection. The other denotations are the same as on Fig.1.

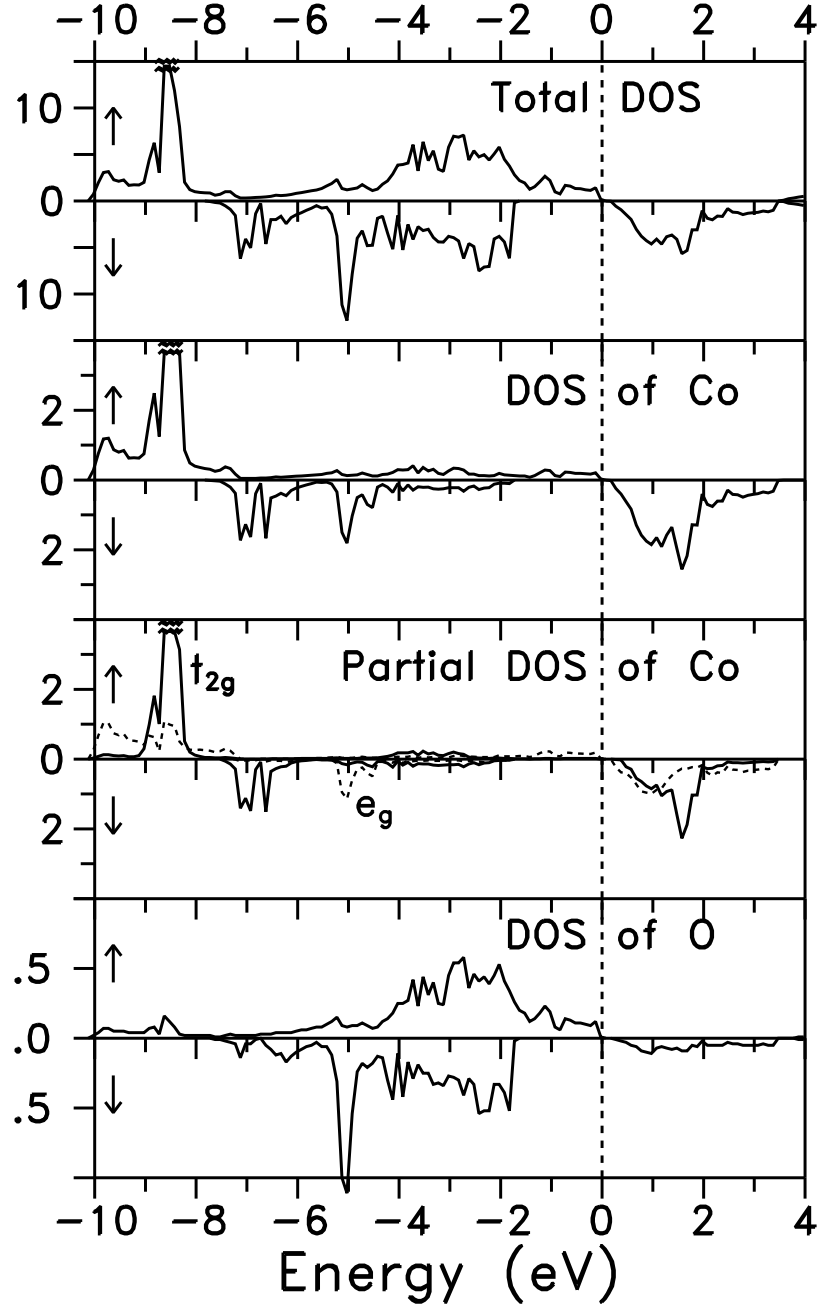


Figure 3: The total and partial densities of states obtained in LDA+U calculations for LaCoO₃ with Co ions in high-spin state ($t_{2g}^4 e_g^2$ configuration). Denotations are the same as on Fig.1 and Fig.2.

photoemission holes in a LS state are mainly formed by oxygen states (note that in Figs.1-3 the partial densities of states of constituent atoms are given per one atom, and there are 3 of oxygen atoms per formula unit). Consequently the final state of the XPS for LS state formally corresponds to $d^6 \underline{L}$ configuration. At the same time the electronic excitations mostly reside on Co e_g orbitals hybridized with p -states of oxygen. However, in the IS case which in our calculations is metallic (Fig.2), the states at the Fermi level contain comparable weight of both Co e_g and O p orbitals.

The IS state obtained is fully polarized which is due to the half-metallic ferromagnetic nature of the solution: the magnetic moment per formula unit is $2 \mu_B$, i.e. it corresponds to the spin $S=1$. In that sense the calculation agrees with the ionic picture, in which the IS configuration of Co is $d^6 (t_{2g}^5 e_g^1)$, with $S=1$.

The IS state of LaCoO_3 in our results turned out to be half-metal [18] ferromagnet, in which only the electrons of one spin projection are at the Fermi level (the other spin subbands are fully occupied). Ferromagnetic arrangement of the magnetic moments may be of course an artifact of the scheme used. In principle, LDA+U method is intended to describe the local correlation effects such as formation of the Hubbard gaps and local magnetic moments, which should still be present in the paramagnetic phase. However technically in the calculations we have to assume certain long-range magnetic order in accordance with translation symmetry of the crystal. What the results obtained in such a way do really tell you, is whether there is a gap or not and what is the value of the *local* magnetic moment.

Although the IS state in the calculations turns out to be metallic, the density of states at the Fermi level is very low, $n(E_F)=0.36$ states per eV per one formula unit. This probably indicates that it would not be so difficult to make this state semiconducting, see the discussion below (section 3.2).

The results presented above show that the first excited configuration – that with the IS – lies only 0.24 eV higher than the ground state with the LS. Experimentally it is established that there is a transition from LS nonmagnetic state to the magnetic one with the increase of temperature. According to the Ref.[2] this transition occurs in the vicinity of 90 K. As the closest magnetic state is that with the IS (HS state lies, according to our results, much higher at 0.65 eV), we ascribe nonmagnetic – magnetic transition in LaCoO_3 to the LS – IS transition.

It is well known (see, e.g., [1]) that Co in the HS state has larger ionic radii than in LS one, and LS – HS transitions are accompanied by the increase of the volume (and vice versa). Keeping that in mind we carried out the calculations of the electronic structure of LaCoO_3 at different lattice parameters which can imitate the influence of the temperature (via thermal expansion). Fig.4 demonstrates the values of total energies for various spin states of Co relative to the energy of $t_{2g}^6 e_g^0$ state at the lattice parameter corresponding to 4 K. In this figure actual lattice parameters used in calculations are shown on the horizontal axis together with the temperature scale (we used the lattice parameters as a function of the temperature measured in Ref.[3]). One sees that with the increase of the specific volume (or with the increase of temperature) the energy of the IS state crosses that of the LS state, which corresponds to the LS – IS transition. In our calculation this crossover occurs at about 150 K – somewhat larger than the experimental value about 90 K. Nevertheless this transition temperature is correct by order of magnitude which for such *ab initio* calculations is rather satisfactory. Note that the HS state still lies high enough even at the temperatures about 600 K although we can not exclude that it could have become the ground state at still larger specific volumes or temperatures.

The total energy for all three solutions (LS, IS, and HS) decreases with the increasing volume and minima are achieved only for lattice parameters corresponding to high temperature. At this value of the volume the total energy of the IS state is lightly lower than LS. It is well known that the equilibrium values of volume calculated with LSDA are always a few percent less than the experimental volume, because LSDA overestimates cohesion. LSDA+U, on the other hand, underestimates cohesion due to its treating the d states as localized. In both cases the calculated lattice parameters significantly deviate from the experimental values. Goodenough suggested that the magnetic transition in LaCoO_3 is caused by the fact that the crystal-field energy δ_{cf} is only slightly larger than the intra-atomic (Hund) exchange energy δ_{ex} . The crystal-field energy is determined by the $3d-2p$ hopping parameters, which strongly depend on crystal volume. Hence if one will perform calculations with lattice parameters corresponding to the equilibrium volume, then the delicate balance between the δ_{cf} and δ_{ex} . Our results show that for low-temperature lattice parameters is larger δ_{cf} than the δ_{ex} , but already a small

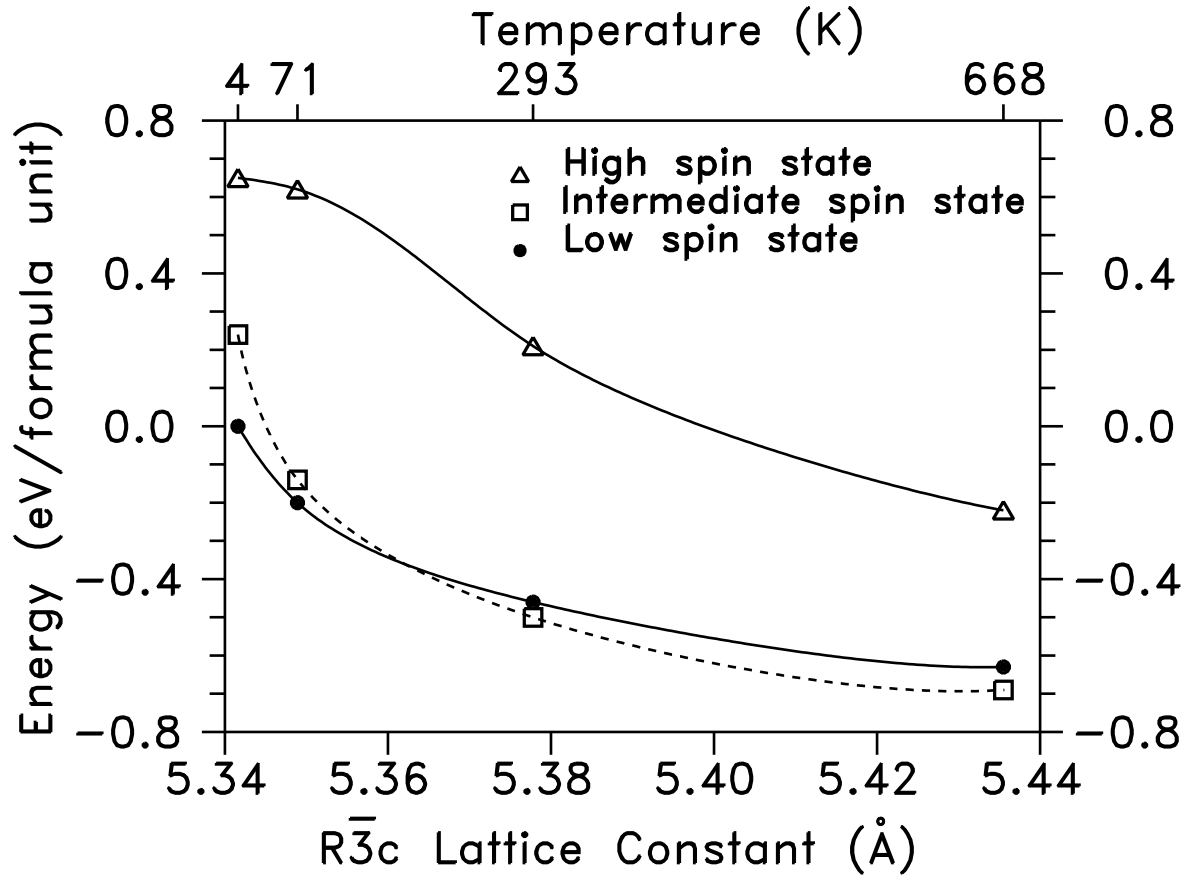


Figure 4: The total energies for various spin states of LaCoO_3 relative to the energy of $t_{2g}^6 e_g^0$ state at 4 K versus $R\bar{3}c$ lattice constant. The correspondent temperatures are marked also.

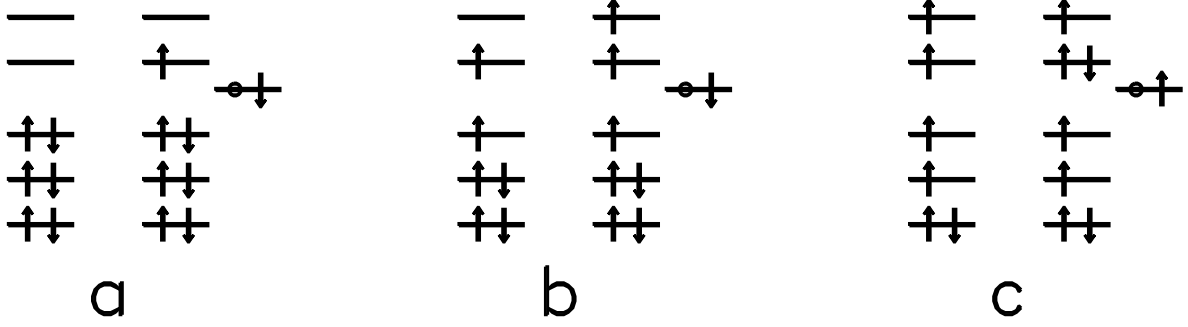


Figure 5: Scheme representation of various Co $d^6 + d^7 \underline{L}$ configurations in low- (a), intermediate- (b) and high- (c) spin states. Open circle denotes a hole in oxygen p -shell.

increase on volume (corresponding to increasing the temperature to 150 K) would reverse this ratio.

Thus from the results obtained we conclude that the nonmagnetic – magnetic transition in LaCoO_3 most probably occurs not between LS and HS states, but between *low*- and *intermediate*-spin states. The reason for the stabilization of the IS state may be understood from the following consideration. Different configurations of Co^{3+} (d^6) are illustrated in Fig.5. Here t_{2g} and e_g are atomic d -states splitted by the crystal field (the splitting $\Delta=10 \text{ Dq}$). In purely ionic picture one should expect that, depending on the ratio between Δ and intraatomic exchange interaction J either LS or HS states should be stable (if the energy of the LS state E_{LS} is taken to be zero, then $E_{IS}=\Delta-J$ and $E_{HS}=2\Delta-6J$, so that LS state is the ground state for $\Delta > 3J$ and HS state – if $\Delta < 3J$; IS state in this scheme always would lie higher). However, as we mentioned in the Introduction, the oxides with unusually high valence of transition metals have a tendency to have the d -shell occupancy corresponding to a lower valence, with the extra hole being predominantly located on oxygen (one gets a configuration $d^7 \underline{L}$ instead of d^6). In this situation the d - p hybridization is especially strong and plays a crucial role. These considerations are also supported by our calculations, see Table 2.

Especially important is the hybridization with the e_g orbitals. One can show that it is stronger for the IS state than for the HS one: there are more channels of p - e_g hybridization in this case (the most favorable configurations of the type $d^7 \underline{L}$, admixed to d^6 , are also shown in Fig.5). In other words, if these configurations ($d^7 \underline{L}$) would be dominant, then the state corresponding to the ground state of the d^7 configuration would have lowest energy – and it is known that for d^7 (Co^{2+}) it is just the configuration of Fig.5b – i.e., the one giving a total state of IS. That is the physical reason why the IS configuration lies below the HS one and may become the ground state for an expanded lattice (higher temperatures).

The nonmagnetic – magnetic transition occurring at $\sim 90 \text{ K}$ which we now associate with the LS – IS transition, is described quite reasonably by our model. The transition temperature obtained in our calculations ($\sim 150 \text{ K}$) lies not so far from that experimentally observed. In Ref.[2] the relative change of the lattice parameter (Δa) at this transition was fitted by the relation (see [19])

$$\Delta a = \frac{\nu * \exp(-E_q/kT)}{1 + \nu * \exp(-E_q/kT)}, \quad (8)$$

where E_q is the energy gap (it was taken in [2] as a fitting parameter), and ν is degeneracy of the magnetic state. As the high-temperature magnetic ground state was believed to be the HS state in Ref.[2], the degeneracy was taken $\nu=15$ (triply degenerated t_{2g} orbital times the spin degeneracy $(2S+1)$ with $S=2$, see Fig.5c). In our

new interpretation the degeneracy will be $\nu=18$ (triply degenerated t_{2g} orbital times double degeneracy of e_g orbital times $(2S+1)$ with $S=1$, see Fig.5b). Thus the fit of Δa would be as successful with this interpretation as with the one given in [2], with actually nearly the same value of the energy gap E_g .

The picture of an IS state can also help to resolve one more problem mentioned in Ref.[2]: that the correlations between magnetic sites in LaCoO_3 are not antiferromagnetic but (weakly) ferromagnetic. One should expect only antiferromagnetic correlations between *high-spin* Co^{3+} ions in which the e_g -shell is half-filled (e_g^2). However in IS Co ions have nominally e_g^1 configuration, and especially if these e_g orbitals are ordered (see discussion below) one can have a ferromagnetic exchange interaction (the well-known example is e.g. ferromagnetic K_2CuF_4 [20]).

3.2 Possible Orbital Ordering in LaCoO_3

The conception of LS – IS transition describes quite reasonably the nonmagnetic – magnetic transition observed in LaCoO_3 . At the same time it was established that the first transition at ~ 90 K leaves this compound semiconducting whereas our calculated IS has a metallic character of the energy spectrum. Is it possible to overcome this disagreement?

As is clear from Fig.5b, the IS state has a strong double-degeneracy (e_g^1 configuration). For localized electrons it would be the typical Jahn-Teller situation. In particular for KCuF_3 it was proposed in Ref.[20] and it was confirmed by calculations in Ref.[21] that there exist the special kind of orbital and magnetic ordering of d -ions in simple cubic lattice with one electron or hole on doubly-degenerate e_g level. The situation in IS LaCoO_3 is very similar to the case of KCuF_3 (keeping in mind that there exist permanent rhombohedral distortion and there are already two Co ions in an elementary cell in LaCoO_3 , the "antiferro" orbital ordering may be consistent with the existing structural data).

We checked this possibility by repeating the calculations, assuming now that there exist an orbital ordering. The structure of the corresponding ordered IS state was taken as consisting of ferromagnetic planes (001) whereas the direction of spins is opposite in the nearest planes. The occupied e_g orbitals were assumed to alternate; as a starting point the orbitals in two sublattices were taken as $d_{x^2-z^2}$ and $d_{y^2-z^2}$, see Fig.6. To supplement this Figure with the information about the other d -orbitals, let's consider the Co ion in $t_{2g}^5 e_g^1$ configuration which has $d_{y^2-z^2}^\uparrow$ occupied e_g orbital (corresponding site is marked as **1** on Fig.6). For this state the other three e_g orbitals are empty and all the t_{2g} orbitals are occupied, with the exclusion of d_{yz}^\downarrow one. This choice minimizes the Coulomb interaction energy of t_{2g} and e_g electrons. For the neighboring Co ion (site **2** in Fig.6) the e_g electron is placed in $d_{x^2-z^2}^\uparrow$ orbital and t_{2g} hole is placed in d_{xz}^\downarrow orbital. Calculations were made for the real rhombohedral crystal structure with lattice parameters corresponding to 71 K. With this state as a starting point the self-consistent calculation was now carried out. The resulting densities of states corresponding to such orbital ordered IS state are presented in Fig.7.

First of all it is necessary to point out that such kind of spin and orbital ordering is stable with respect to the self-consistency iterations and hence there exists the solution with such symmetry. The character of an energy spectrum turned out to be gapless semiconducting-like. The wide e_g band which crossed the Fermi level in the case of IS state without orbital order (see Fig.2) is now splitted. The top of the valence band is formed (for one sublattice, e.g. for Co site **1**) by $d_{y^2-z^2}$ states and the bottom of conduction band – by $d_{3x^2-r^2}$ states (Fig.7b,c) hybridized with the oxygen states. As to the t_{2g} densities of states, the character of their energy distribution is practically not changed in comparison with the case of IS state without orbital ordering. The value of spin magnetic moment of Co is $1.87 \mu_B$ in this orbitally ordered IS state and it is less than for one without orbital order ($2.11 \mu_B$).

When we compare the two IS states with the fixed spin magnetic moment $1.87 \mu_B$, the total energy of the orbitally ordered IS state is 0.11 eV lower. The necessity of using a fixed magnetic moment is due to the limitation of the band structure scheme. The magnetic state of LaCoO_3 is known to be paramagnetic (with the possible short-range spin or orbital ordering). At the same time as we already mentioned above, it is necessary to set a long-range magnetic order in calculations (antiferromagnetic for orbitally ordered IS state and ferromagnetic for one without orbital order). This long-range magnetic ordering imposed (in addition to the intraatomic exchange) influences somehow both the local magnetic moment and the total energy. In the case of long-range

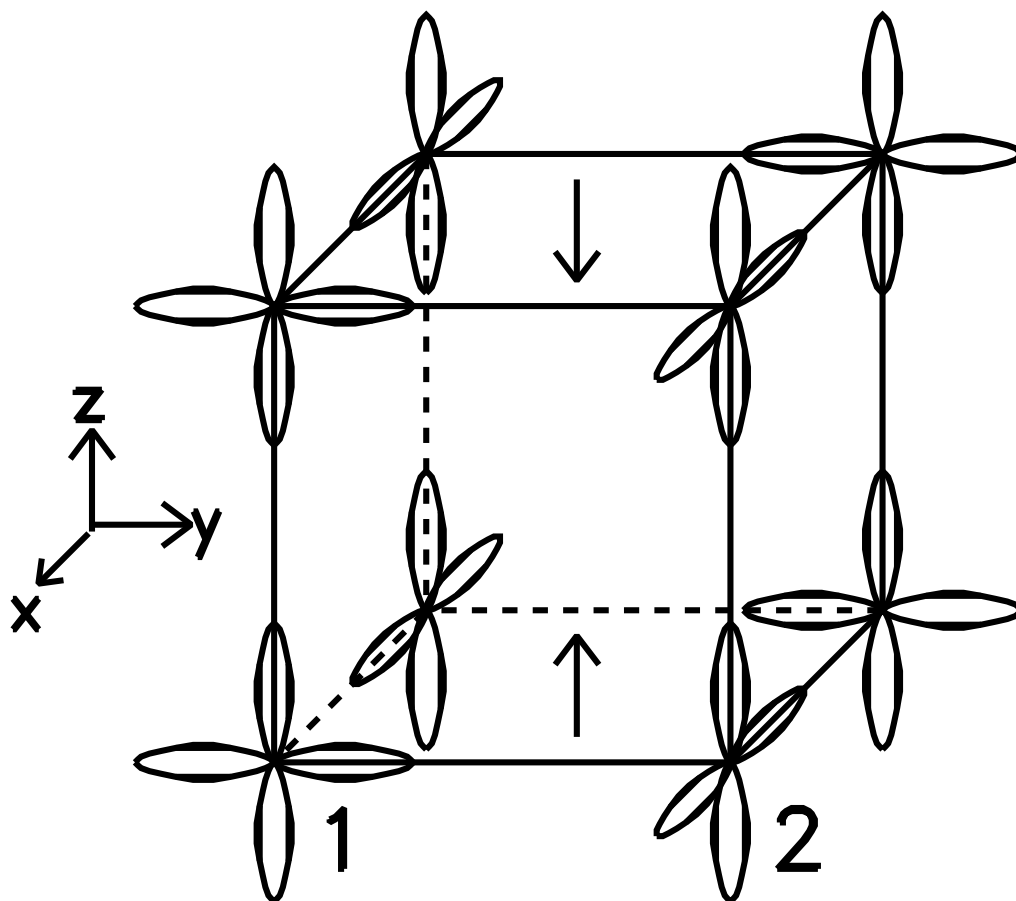


Figure 6: Spin and orbital ordering in orbital ordered intermediate spin state for occupied e_g orbitals. For the simplicity the perfect cubic structure for Co ions is shown.

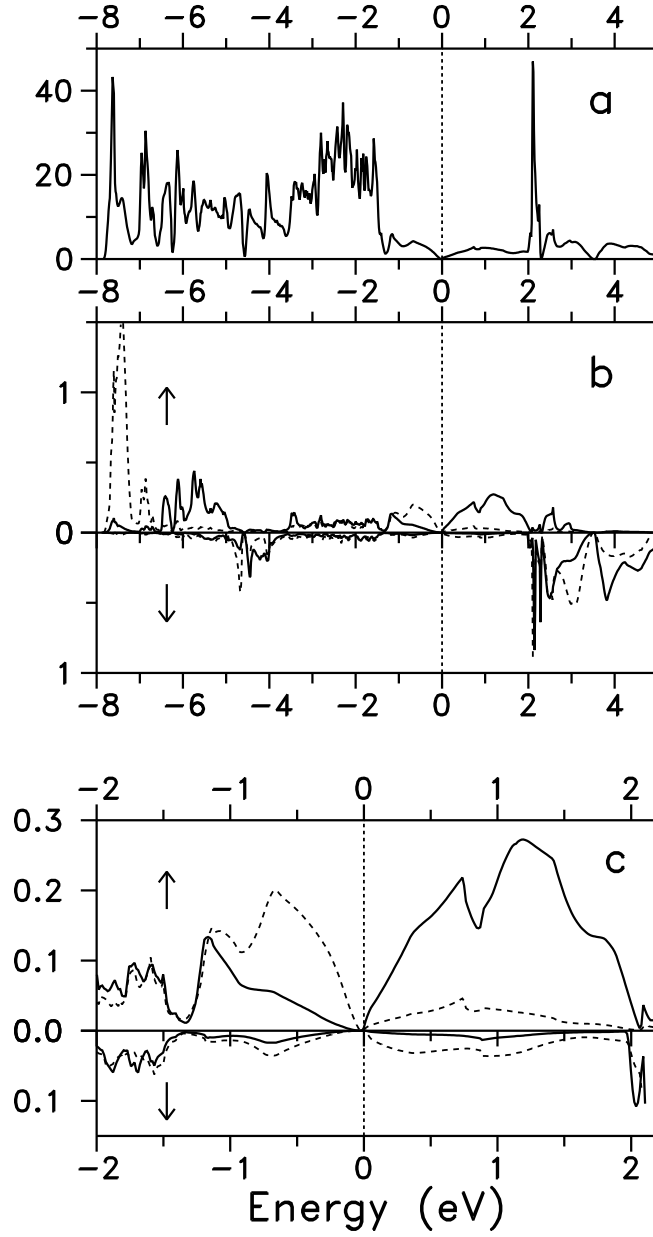


Figure 7: The total and partial densities of states obtained in LDA+U calculations for LaCoO₃ with Co ions in ordered intermediate-spin state. **a:** Total density of states (per 4 formula units and both spins); **b:** partial Co *e_g* densities of states e.g. for Co site **1** in Fig.6: solid line - for *d_{y²-z²}* states, dashed line - for *d_{3x²-r²}* states; **c:** the same as in **b** in the vicinity of the Fermi level. Denotations are the same as on Fig.2.

antiferromagnetic order the value of the magnetic moment is apparently underestimated in comparison with the real paramagnetic state, for the ferromagnetic one – overestimated. Thus to estimate the relative stability of different phases we compare the energies calculated for the same value of the magnetic moment. Our calculations show that in the case of equal spin values the orbitally ordered IS state is more preferable than the one without orbital order.

One can interpret now the first nonmagnetic – magnetic transition (at about 90 K) as a transition of Co ions from LS to IS state with the specific orbital ordering of occupied e_g orbitals. Our results show that this transition occurs at temperatures lower than 150 K. Under this transition a magnetic moment on Co sites appears whereas the material is still nonmetallic. The spin-only value of the *effective* magnetic moment, in the case of IS state ($S=1$), is $\mu_{eff}=2.83 \mu_B$ – somewhat below experimental value of 3.1–3.4 μ_B . It will be increased by the orbital contribution, because there is in principle an unquenched moment of t_{2g} electrons for the configuration $t_{2g}^5 e_g^1$ (which e.g. for Co^{2+} ions the increases the value of μ_{eff} typically by $\sim 0.3 \mu_B$). We cannot treat this effect numerically because our codes do not account for the spin-orbit interaction; however we expect on physical grounds that this effect should be present (which, by the way, would change somewhat the occupation of t_{2g} orbitals). An extra change of μ_{eff} may be due to the very strong d - p hybridization which leads to a large contribution to the total wave function of a state $d^7 \underline{L}$ ($t_{2g}^5 e_g^2 \underline{L}$). In this state the effective moment of Co ion is that of the high-spin Co^{2+} ($S=3/2$) compensated by the opposite polarization of the oxygen p -shell ($S=-1/2$) (note that this picture is supported by the calculations (see Table 2) where local Co spin moment is 2.11 μ_B and the total spin moment per unit cell is 2 μ_B). This fact may significantly change the value of μ_{eff} measured in the susceptibility experiments.

The IS state with the nominal configuration $t_{2g}^5 e_g^1$ may have an orbital ordering because of the doubly degenerate e_g orbitals (strong Jahn-Teller nature of this configuration). This turned out to be the case in our calculations: the orbitally ordered state may be crudely described as an alternation of the occupied $d_{z^2-x^2}$ and $d_{z^2-y^2}$ orbitals.

According to our calculations, this ordering leads to the splitting of the e_g (σ^*)-band, leading practically to the zero-gap situation, with the Fermi level lying in the gap. The second gradual transition to the metallic state (~ 600 K) with the increase of the effective magnetic moment value up to $\mu_{eff}=4.0 \mu_B$ may then be associated with the disappearance of the orbital ordering with increased temperature still within the IS state. This IS state without orbital order is calculated to be a metal with a larger magnetic moment. Our calculations show that the second transition has no relations to the HS state of Co ions because the HS solution lies still high in energy and if realized would have been semiconductor.

4 CONCLUSION

The calculations of the electronic structure in LDA+U approximation for LaCoO_3 were performed. At 4 K the lowest total energy has the nonmagnetic insulating solution with Co ions in LS state. Three excited state configurations (two IS and one HS) are also found to be stable, with local magnetic moments on Co sites. The t_{2g} states exhibit narrow bands whilst the e_g states form broad bands. With the increase of lattice parameter corresponding to the thermal lattice expansion two transitions can be expected: the first occurs from LS state to IS state with the orbital ordering which in our calculation is a zero-gap semiconductor. The second transition occurs within the IS state and is connected with gradual disorder of occupied e_g orbitals. We believe that although many details are not clear yet, the concept of the nonmagnetic – magnetic and semiconductor – metal transitions in LaCoO_3 as connected mainly with IS states is a good candidate to explain the properties of this interesting material which remains a puzzle for so long.

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